# UNITED STATES DEPARTMENT OF THE INTERIOR

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Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment

## Molybdenum

Participating Agencies:

Bureau of Reclamation
U.S. Fish and Wildlife Service
U.S. Geological Survey
Bureau of Indian Affairs

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#### CONSTITUENTS OF CONCERN

## Molybdenum

## **Description**

Molybdenum (Mo) is a silver-white metallic element of the second transition series; its atomic number is 42, and its atomic weight is 95.94 (Pais and Jones 1997). It has chemical properties similar to those of chromium. It is commonly used in steel alloys because it imparts hardness, strength, heat resistance (melting point 2,617°C), and corrosion resistance to these alloys. Molybdenum is present in all plant and animal tissues and is considered an essential micronutrient for most life forms (Schroeder et al. 1970; Underwood 1971; Chappell and Peterson 1976; Chappell et al. 1979; Goyer 1986; Eisler 1989).

#### Occurrence

Molybdenum does not occur free in nature and is only found in combination with sulfur, oxygen, tungsten, lead, uranium, iron, magnesium, cobalt, vanadium, bismuth, or calcium. Its principal ore is molybdenite (MoS<sub>2</sub>), "a lead-gray hexagonal mineral . . . [which] resembles graphite in appearance and to the touch, but has a bluer color" (Bates and Jackson 1987). Less important sources include wulfenite (PbMoO<sub>4</sub>), powellite (CaMoO<sub>4</sub>), and molybdophyllite (PbMoSiO<sub>4</sub>). Molybdenum is widely disseminated in the environment: its abundance in the Earth's crust is estimated at 1-1.5 mg/kg (Budaveri 1996); and back-ground concentrations in the United States are 1.2-4.1 μg/L for rivers, <1 μg/L for ground-water, 5–57 mg/kg dw for river sediments, and 1.2 (0.1–40) mg/kg dw for soils (Friberg et al. 1975; Chappell et al. 1979). Molybdenum concentrations in animal tissues are generally highest in liver, followed by kidney, spleen, lung, brain, and muscle (Berman 1980). Total

body molybdenum is present to the largest degree in skeletal tissue (Underwood 1977).

Molybdenum is used primarily in the manufacture of steel alloys for aircraft and weapons. It is also used as an electrode material and as a catalyst in petroleum refining. Most of the recent global production of about 100,000 tons annually comes from the United States. Three mines in Colorado account for nearly 70 percent of domestic pro-duction. Human activities that contribute to molybdenum contamination include the combustion of fossil fuels, and smelting, mining, and milling operations for steel, copper, and uranium.

## **Summary of Effects**

Table 26 summarizes the predicted effects of environmental exposures to molybdenum, based on the limited information currently available.

## **Study Approaches**

The majority of papers reviewed for this report were laboratory studies dealing with molybdenum effects on mammals and poultry. Mammalian literature consisted of studies done on domestic animals, primarily rats, and was published from the late 1940's to early 1960's. Avian literature consisted exclusively of poultry studies published in the late 1950's to early 1960's. For aquatic species, the literature was composed primarily of freshwater laboratory studies and offered little information about fish, invertebrates, amphibians, or reptiles. The review adequately addressed the formally published scientific

Table 26.—Predicted molybdenum effect levels

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Media	No effect	Level of concern	Toxicity threshold	Explanation
Water (mg/L)	0.02	0.02-0.12	0.12	For fish. 0.02, upper limit of natural background (Eisler 1989); 0.12, LC10 for larval trout (Birge et al. 1980)
·	0.02	0.02-0.96	0.96	For amphibians. 0.02, upper limit of natural background (Eisler 1989); 0.96, LC50 for larval toads (Birge 1978)
			>50	For plants. Reduced growth of green algae; 96-h exposure
Domestic chickens (mg/kg in feed)		>500	>6,000	Adverse effects on reproduction and on survival, respectively
Bird eggs (mg/kg dw)	23	23-33	<33	Lepore and Miller (1965)
Mammals (Cu:Mo ratio in feed)	6:1-10:1	<2:1 <i>or</i> >10:1		Ratios found to lead to either Cu deficiency or Cu toxicosis

literature, but not the scientific "gray literature," which includes government reports and unpublished studies.

## Abiotic Factors Affecting Bioavailability

#### Water

Natural molybdenum concentrations in ground and surface waters rarely exceed 20  $\mu$ g/L; higher concentrations probably indicate industrial contamination (Eisler 1989). Concentrations in surface waters range from 0.4  $\mu$ g/L in uncontaminated North American rivers to as much as 100,000  $\mu$ g/L in mining wastewater. In the United States, ground-water molybdenum concentrations are usually <1  $\mu$ g/L but have been reported as high as 50,000  $\mu$ g/L near uranium mills in Colorado (Eisler 1989). Molybdenum concentrations in saline water appear to be directly related to salinity (Prange and Kremling 1985; Sloot et al. 1985).

Aquatic organisms are relatively resistant to molybdenum and generally show no adverse effects on growth or survival at water concentrations lower than 50 mg/L (Eisler 1989); however, there are large differences between species in their ability to bioconcentrate molybdenum. Blue-green algae (Anabaena oscillaroides) had a bioconcentration factor (BCF) of 3,300 after 1 hour of exposure at a concentration of 0.005 µg Mo/L (Steeg et al. 1986). The freshwater alga Nitella flexilis and some lake periphyton had BCFs of 628 and 3,570, respectively, in 25 days when placed in a 0.014-µg Mo/L concentration (Short et al. 1971). In a 3.3-mg Mo/L con-centration, crayfish (Pacifastacus leniusculus) had BCFs of 5.7 in muscle and 9.8 in the carapace. High bioconcentration of molyb-denum by certain species of aquatic algae and invertebrates has been recorded without apparent harm to the organism; however, the hazard potential to organisms that feed on the bioconcentrators is not clear (Eisler 1989).

#### Soil

Soils average 1–2 mg/kg molybdenum, although they range from trace concentrations to 40 mg/kg or greater. In the United States,

molybdenum concentrations in soils generally increase from east to west (Adriano 1986; Kubota 1977).

The largest concentrations of molybdenum are found in the 30 cm of soil nearest the surface. Its uptake into certain legumes and other plants may correlate with the soluble molybdenum concentrations in the soil, but this relationship does not occur with all types of plants. Molybdenum uptake by plants can vary dramatically even between different varieties of the same species (Barshad 1948).

#### **Biota**

#### **Plants**

Molybdenum is considered essential for aquatic plant growth, but the concentrations required are not known. Aquatic plants are relatively resistant to molybdenum toxicity. Concentrations observed to cause adverse effects in sensitive species were 50 mg/L for growth and 108 mg/L for development (table 27).

The molybdenum content of some plants has been shown to vary by stage of development, as evidenced by a twofold to threefold increase from spring to fall in leaf and stem concentrations of alfalfa and some grasses. Although older plants may contain more molybdenum, younger plants appear to cause more molybdenosis in animals. This dif-ference may arise because animals consume different parts of young, succulent plants.

#### Fish

Acute toxicity values for molybdenum in the literature (table 27) indicate that it is relatively nontoxic to fish. The one exception was newly fertilized eggs of rainbow trout exposed for 28 days through 4 days posthatch; these had an LC50 of 0.79 mg/L and an LC10 of

0.12 mg/L. In general, molybdenum was more toxic to younger fish than to older fish, although a study by Hamilton and Buhl (1990) found that the 96-hr LC50 values for all Chinook and coho salmon exceeded

1,000 mg/L regardless of the quality of the dilution water (soft, fresh, or brackish) or the life stage tested (eyed egg, alevin, or fry). Moreover, the addition of molybdenum to test mixtures of boron, selenite, and selenate seemed to increase the acute toxicity of these mixtures to Chinook and coho salmon (Hamilton and Buhl 1990).

Few studies have compared the molybdenum concentrations in fish tissues to ambient concentrations, and the toxicological effects of molybdenum in fish tissues are unknown (Eisler 1989; Saiki et al. 1993). As shown in table 27, Ward (1973) found that, in nature, tissue molybdenum concentrations in rainbow trout increased only slightly with increasing water concentrations. Saiki et al. (1992) confirmed Ward's observations in controlled experiments. An eightfold range of waterborne molybdenum caused very little variation in the concentration of molybdenum in tissues of juvenile Chinook salmon or striped bass.

#### **Birds**

There are no data showing molybdenum's effects on wild birds. In domestic birds, adverse effects have been reported for growth at dietary molybdenum levels >200 mg/kg, for reproduction at 500 mg/kg, and for survival at 6,000 mg/kg (Eisler 1989). Poor growth was the only symptom of molyb-denum toxicity noted by Miller and Denton (1959) even at 2,250 mg Mo/kg added to the diet. In all groups in which the level of added molybdenum inhibited growth, inorganic sulfate alleviated part of the growth inhibition. The addition of inorganic sulfate caused a considerable decrease in the molybdenum content of liver tissues. Liver molybdenum

Table 27.—Effects of molybdenum on living organisms as reported in published studies

Species	Mo con- centration (mg/L <i>or</i> mg/kg)	Where measured	Effects	Reference	
Plants					
Euglena gracilis	108 Water		Abnormal development	Colmano 1973	
	>960		No growth		
Green algae, Chlorella vulgaris	50	Water	Reduced growth after 96 h	Sakaguchi et al. 1981	
Invertebrates					
Amphipod,	2,650	Soft water	96-h LC50	Martin and Holdich 1986	
Crangonyx pseudogracilis	3,618		48-h LC50		
Hermit crab, Eupa- gurua bernhardus	222	Water	48-h LC50	Abbott 1977	
Fish		•			
Chinook and coho salmon (eyed eggs, alevins, and fry)	>1,000	Fresh, brack- ish and soft water	96-h LC50	Hamilton and Buhl 1990	
Fathead minnow, Pimephales promelas	70	Soft water	96-h LC50	McConnell 1977	
	360	Hard water			
Rainbow trout, Oncorhynchus mykiss	Trace	Water	Mo in tissue 5-11'8 µg/kg ww	Ward 1973	
	6		Mo in tissue 10-146 µg/kg ww		
	300		Mo in tissue 13-332 µg/kg ww		
	800		96-h LC50 (20-mm size class)	McConnell 1977	
	1,320		96-h LC50 (55-mm size class)		
Rainbow trout	0.12	Moderately	28-d LC10	Birge et al. 1980	
(fertilization through 4 days post-hatch)	0.79	hard water	28-d LC50		
Sheepshead minnow, Cyprindon variegatus	3,057	Water	96-h LC50	Knothe and Van Riper 1988	
Amphibians		•			
Frogs	2,000	Water	Zone of toxic action	Venchikov and Kaprielov 1976	

Table 27.—Effects of molybdenum on living organisms as reported in published studies—Continued

Species	Mo con- centration (mg/L <i>or</i> mg/kg)	Where measured	Effects	Reference	
Birds					
Chicken	2,250 Mo	Dietary; basal diet 0.25%	Body weight 37% that of control chicks	Miller and Denton 1959	
	2,250 Mo + 13,200 sulfate	sulfur, 3.3 ppm Mo, and 13 ppm Cu	Body weight 72% that of control chicks		
	750 Mo + 2,200 sulfate		Decrease in Mo content in liver tissues of chicks		
Chicken (chicks)	200 (sodium molybdate)	Diet	Reduced growth after 56 d	Arthur et al. 1958	
	300 (sodium molybdate dihydrate)	Diet	25% reduced growth after 24 d	Kratzer 1952	
	500 (sodium molybdate dihydrate)	High-sulfate purified diet	Minimum toxic dose after 28 d; lowest concentration depressing growth	Davies et al. 1960	
Turkey (poults)	300 (sodium molybdate dihydrate)	Diet	25% reduced growth after 24 d	Kratzer 1952	
Mammals			<del>-</del> .	<del>1</del>	
Cattle, Bos spp.	60	Diet	Low Cu in liver; intestinal disturbances; brittle bones prone to fracture	Penumarthy and Oehme 1978	
Cattle (lactating cows)	40 Mo, 6 Cu	Diet	30% reduction in milk yield after 63 d; rapid decline in plasma copper; milk Mo levels 1.6 ppm; growth reduction in nursing calves	Wittenberg and Devlin 1987	
Mouse (Mus sp.)	10	Drinking water	Decrease in survival of 2d and 3d generations	Earl and Vish 1979	
Mule deer	2,500 (sodium molybdate)	Diet	Weight loss after 27 d	Ward and Nagy 1976	
·	5,000 (sodium molybdate)		Reduced feeding after 14 d		
Rat	. 80 '	Cu-deficient diet	Inhibited growth and reduced survival	Underwood 1971, 1979	
	5000	Diet	Lethal in 2 weeks	Chappell et al. 1979; Friberg et al. 1975	

Table 27.—Effects of molybdenum on living organisms as reported in published studies—Continued

Species	Mo con- centration (mg/L <i>or</i> mg/kg)	Where measured	Effects	Reference
Mammals—Continue	d			
Rabbit ( <i>Oryctolagus</i> sp.)	100	Diet .	Reduced growth, hair loss, dermatosis, anemia, skeletal and joint deformities (lifetime exposure)	Chappell et al. 1979
	1000	Diet	Weight and hair loss, leg deformities, dermatosis, anemia, death (28 d)	Arrington and Davis 1953
	2,000-4,000	Diet	Many deaths of weanlings in 37 d, adults in 53 d; survivors were anorexic, diarrhetic, anemic, and had front leg abnormalities	Friberg et al. 1975; Arrington and Davis 1953
Sheep, <i>Ovis</i> spp.	~5.5–12.5	Grazing pastures treated with 420 g Mo/ha at start, week 45, and week 72	Lameness, connective tissue lesions in most sheep; Mo concentrations (mg/kg fw): plasma 1.7, liver 6.0–6.4; kidney 6.9–8.1	
Sheep (lambs)	Cu:Mo < 0.4	Soil	15-39% swayback	Friberg and Lener 1986

concentrations of 22-36 mg/kg dw (6–10 mg/kg ww) have been correlated with toxic effects in domestic birds (Puls 1988). When copper was added to the diet, in addition to molybdenum and inorganic sulfate, a further reduction in molybdenum liver tissue concentrations was observed. These studies show that the amount of molybdenum stored by the liver tissues is dependent upon the amount in the diet and upon the ratios of molybdenum, copper, and sulfate in the diet. Increasing the molybdenum content of the diet increased the copper storage of the liver.

Avian eggs normally contain <1 mg Mo/kg (dry weight basis), averaging about 0.25 mg Mo/kg (Romanoff and Romanoff 1949). Lepore and Miller (1965) studied the effects of maternally deposited molybdenum content on the viability (i.e., hatchability) of eggs laid by White Rock

chickens. They observed normal egg viability up to about 23 mg Mo/kg in the egg (dry weight basis). At 33 mg/kg, about 50 percent of the eggs were inviable (i.e., the approximate EC50). Thus, the threshold for avian embryotoxicity occurs between 23 and 33 mg Mo/kg egg (dry weight basis). The EC100 concentration was approximately 60 mg/kg. Based on transfer rates of molybdenum from the maternal diet to the eggs, as documented by Lepore and Miller (1965) and Motzok et al. (1957), the dietary threshold for reproductive impairment lies somewhere between 100 and 500 mg Mo/kg (dry feed basis). This suggests that, in the absence of significant interaction effects, molybdenuminduced avian embryotoxicity in the field may be very rare. Lynch et al. (1988) reported that even downstream from spills of molybdenum mill tailings in the Red River of New Mexico,

#### **Interactions**

Molybdenum toxicological properties are governed to a large extent by interactions with copper and sulfur, but interactions with other metals and compounds may confound this interrelation. For molybdenum, interactions are so dominant that a particular level of intake in an animal's diet can lead to either molybdenum deficiency or toxicity, depending on the relative intakes of copper and inorganic sulfur (Schroeder et al. 1970; Underwood 1971, 1979; Clawson et al. 1972; Suttle 1973, 1983; Friberg et al. 1975; Buck 1978; Friberg and Lener 1986; Goyer 1986; Kincaid et al. 1986; and others cited in Eisler 1989). A low copper-tomolybdenum ratio (<2), rather than the absolute dietary concen-tration of molybdenum, is the primary determinant of an organism's susceptibility to molybdenum poisoning. The first indications of the interaction between copper and molybdenum came from England more than 40 years ago, when cattle grazing on herbage rich in molybdenum developed molybdenosis. Molybdenosis is not expected to occur in animals when the copper-tomolybdenum ratio is near 5 (Buck 1978; Ward 1978; Mills and Bremner 1980).

On the other hand, studies of molybdenum metabolism are of limited value unless the status of inorganic sulfate in the diet is known (Underwood 1971, 1979); inorganic sulfate alleviates molybdenum toxicity by increasing molybdenum excretion. Molybdenum levels in animal tissues give little indication of the dietary molybdenum status and are of little value for diagnosing molybdenum toxicity unless the sulfate, protein, and copper status of the diet are also known (Eisler 1989).

### **Regulatory Standards**

U.S. Environmental Protection Agency standards and criteria [See Appendix II for explanation of terms. Source: EPA 1995]				
Status	Listed for regulation; carcinogenicity unknown.			
Drinking water MCL	None established			
Drinking-water health advisories for 70-kg adult	Reference dose: Long-term HA: Lifetime HA: DWEL:	5 µg/kg/day 50 µg/L 40 µg/L 200 µg/L		

No regulatory standards currently exist for the protection of fish and wildlife from dietary exposure to molybdenum. Molybdenum is not an EPA priority pollutant, and no national water-quality criteria for the protection of freshwater aquatic life have been developed. For standards and criteria set by State agencies, contact those agencies directly. See Appendix I for a listing of water-quality officials in the 17 Western States.

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